



A new lithium salt with tetrafluoro-1,2-benzenediolato and oxalato complexes of boron for lithium battery electrolytes

Xiao-Yan Li^a, Zhao-Ming Xue^{a,*}, Jun-Fei Zhao^b, Chun-Hua Chen^c

^a Department of Chemistry, Anhui University, Hefei, Anhui 230039, PR China

^b Department of Chemistry, Hefei Normal University, Hefei, Anhui 230601, PR China

^c Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China

HIGHLIGHTS

- ▶ A new lithium salt (4FLBDOB) is synthesized.
- ▶ The salt is thermally stable and soluble in organic solvents used in batteries.
- ▶ Correlation between the HOMO energy and the electrochemical stability is established.
- ▶ The new lithium salt (4FLBDOB) has better battery performances than LBDOB and FLBDOB.

ARTICLE INFO

Article history:

Received 13 October 2012

Received in revised form

30 January 2013

Accepted 2 February 2013

Available online 9 February 2013

Keywords:

Lithium [tetrafluoro-1,2-benzenediolato

(2-)-o,o' oxalato]borate

Electrolytes

Li-ion battery

Electrochemistry

ABSTRACT

A new unsymmetrical lithium salt containing $C_2O_4^{2-}$ [dianion of oxalic acid], $C_6O_2F_4^{2-}$ [dianion of tetrafluoro-1,2-benzenediol], lithium [tetrafluoro-1,2-benzenediolato(2-)-o,o' oxalato]borate (4FLBDOB) is synthesized and characterized. The thermal characteristics of it, and its derivatives, lithium [3-fluoro-1,2-benzenediolato(2-)-o,o' oxalato]borate (FLBDOB), lithium [1,2-benzenediolato(2-)-O,O' oxalato]borate (LBDOB), and lithium bis[oxalato]borate (LBOB) are examined by thermogravimetric analysis (TG). The thermal decomposition in air begins at 302 °C, 272 °C, 262 °C and 256 °C for LBOB, 4FLBDOB, FLBDOB and LBDOB respectively. The order of the stability toward oxidation of these organoborates is LBOB > 4FLBDOB > FLBDOB > LBDOB, which is in the same order of the thermal stability. The cyclic voltammetry study shows that the 4FLBDOB solution in PC is stable up to 4.0 V versus Li^+/Li . They are soluble in common organic solvents. Ionic dissociation properties of 4FLBDOB and its derivatives are examined by conductivity measurements in PC + THF, PC + DME, EC + THF, and EC + DME (molar ratio 1:1) solutions. Among the series of LBDOB, FLBDOB and 4FLBDOB, the new lithium salt (4FLBDOB) has the best battery performances.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Many researchers have attempted to develop improved electrolytes for lithium batteries with high energy density and long cycle life [1–5] as power sources for portable electronic instruments and electric vehicles in order to protect the environment and natural resources. Barthel et al. reported a new class of electrochemically and thermally stable lithium salts [6,7] with a chelate-type boron-containing anion, such as lithium bis[3-fluoro-1,2-benzenediolato(2-)-O,O]borate (FLBBB) [8], lithium bis[tetrafluoro-1,2-benzenediolato(2-)-o,o] borate (4FLBBB) [9]. Xu et al.

also reported lithium bis(oxalato) borate (LBOB) and lithium [malonato oxalato]borate (LMOB) as advanced electrolytes for Li-ion battery [10,11]. The common feature of these anions is that extensive charge delocalization is present in them because they are composed of strongly electron-withdrawing substituents. Thus, the lithium salts of these anions yield sufficiently high ionic conductivity in solutions, which exhibit wide electrochemical stability windows and good thermal stability.

According to our previous theoretical studies [12–17], the pronounced charge delocalization anions, $C_2O_4^{2-}$ [dianion of oxalic acid] and $C_6O_2F_4^{2-}$ [dianion of tetrafluoro-1,2-benzenediol], were chosen as the unsymmetrical chelators to coordinate with boron to form lithium salt in this study to further our understanding the relationship between property and structure of these lithium salts. A new lithium salt, lithium [(tetrafluoro-1,2-benzenediolato(2-

* Corresponding author. Fax: +86 551 3861338.

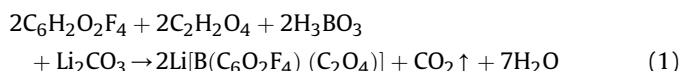
E-mail address: zmxue@ahu.edu.cn (Z.-M. Xue).

)-o,o' oxalato]]borate (4FLBDOB), as shown in Fig. 1, was synthesized. Its thermal and electrochemical stabilities, conductivities in some solvent mixtures were studied and compared with those in the FLBDOB, LBDOB and LBOB electrolytes.

To further our understanding the properties of this new lithium salt at a quantum chemistry level, the density functional theory (DFT) B3LYP method [18,19] was chosen. We will address the relationship between molecular structures and properties regarding the 4FLBDOB[−], FBDOB[−], BDOB[−] and BOB[−] anions and their lithium salts.

2. Experimental and computational methods

4FLBDOB was synthesized according to reaction (1).



Specifically, 0.02 mol oxalic acid, 0.02 mol tetrafluoro-1,2-benzenediol [9], 0.01 mol lithium carbonate, 0.02 mol boric acid, and 20 ml distilled water were placed in a flask with stirrer and water separator and rinsed with high-purity nitrogen. The heterogeneous mixture was slowly heated to 60 °C under purified nitrogen. Within an hour, no significant formation of gas could be established. Thereupon, 20 ml toluene was added. The reaction mixture was then slowly heated to azeotropic point where a clear white solution was obtained. After removing 22.5 ml water from the solution within 20 h and cooling down to room temperature, a Gray white precipitate was observed. It was purified by multi-time recrystallization by dissolving into acetonitrile (AN) and drying in vacuo at 90 °C for 24 h followed by 110 °C for 48 h. After drying in vacuo, the product was translated into glove box. The yield for the purified salt was up to 79%. The purity of the compound was examined by inductively coupled plasma (ICP) analysis for Li and B contents, which were measured as Li 2.45% and B 3.72%. These data were close to the calculated values Li 2.43% and B 3.78% for 4FLBDOB. The ¹³C NMR spectra of the prepared solid in dimethyl sulfoxide (DMSO-*d*₆) gave four signals at chemical shifts of 152.01 (C1/C6), 117.76 (C5/C6), 108.072 (C3/C4), 158.60 (C7/C8) ppm. ¹¹B (referenced to BF₃·Et₂O) NMR spectra gave one signal at chemical shifts of 19.75 ppm. ⁷Li (referenced to LiNO₃) NMR spectra gave one signal at chemical shifts of 0.15 ppm.

The X-ray tests of precursors and salts, 4FLBDOB, are arranged, as shown in Fig. 2. Comparing the peaks of 4FLBDOB, H₂C₂O₄, C₆H₂O₂F₄ and LiCO₃, we can get the result that the prepared compound is pure 4FLBDOB, not the precursors.

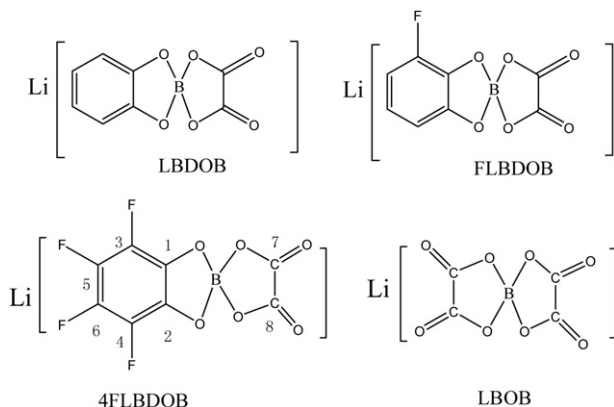


Fig. 1. Structure of LBDob, FLBDob, 4FLBDob and LBOb.

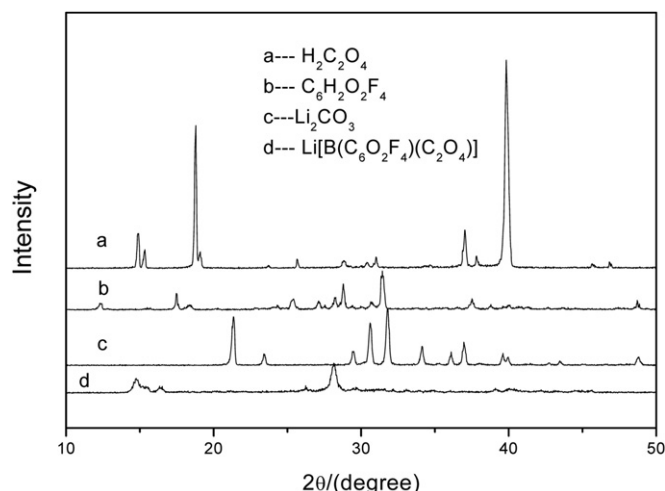


Fig. 2. XRD patterns of 4FLBDOB and their precursors.

On the other hands, comparing the peaks of the ¹³C NMR spectra of the prepared solid 4FLBDOB, and LBOB, in dimethyl sulfoxide (DMSO-*d*₆), we know that the prepared compound is pure 4FLBDOB, and not 4FLBDOB or LBOB. 4FLBDOB gives four signals at chemical shifts of 152.01 (C1/C2), 117.76 (C3/C4), 108.072 (C5/C6), 158.60 (C7/C8) ppm. Bis(fluoro-1, 2-benzenediolato) boron (4FLBDOB) [9] gives 135.3 (C1/C2), 134.0 (C3/C4), 132.7 (C5/C6) ppm. LBOB [10] gives 158.1 ppm. Comparing the peaks of the ¹¹B NMR spectra of the prepared solid in dimethyl sulfoxide (DMSO-*d*₆), we also know that the prepared compounds is pure 4FLBDOB, not the 4FLBDOB or LBOB. ¹¹B (referenced to BF₃·Et₂O) NMR spectra of 4FLBDOB, 4FLBDOB, and LBOB gives one signal at chemical shifts of 19.7, 15.6, 12.0 ppm, respectively.

The procedures of synthesis FLBDOB [20], LBDOB [21], LBOB were described previously.

The purification procedures for propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), and tetrahydrofuran (THF), as well as the electrochemical equipment for electrochemical studies, are given in Refs. [9] and [10].

Thermogravimetric (TG) analysis of the LBOB, 4FLBDOB, FLBDOB, LBDOB was carried out with Perkin–Elmer Pyres-1 DMDA-V1 model, using a sample of about 10 mg. The NMR spectra were measured with AV-400 (Bruker, 9.40 T, 400.13 MHz ¹H NMR). Inductively coupled plasma (ICP) emission spectrometry for both Li and B (model Poasma-Spec). The decomposition voltages (*i*–*E* curves) of the electrolytes using a three-electrode system (platinum wire, surface area 4.91 × 10^{−4} cm², working, Li plate counter, and Li plate reference electrodes) were measured at a scan rate of 9 mV s^{−1}. Preparation of the electrolyte solutions and the cell assembly were carried out in a glove box (Labmaster 130, MBRAUN) at low water (<1 ppm), and oxygen (<1 ppm) contents.

The local minima of the complexes have been fully optimized by analytic gradient techniques. The method used was the density functional theory (DFT) with Becke's three parameters (B3) exchange functional along with the Lee–Yang–Parr (LYP) non-local correlation functional (B3LYP). All of the complexes were treated with DFT method at B3LYP/6-31 ++ G(2df,2p) level for full geometry optimization.

Single-point energy calculations at higher level basis set (B3LYP/6-311 ++ G(3df, 3pd))/B3LYP/6-31 ++ G(2df,2p)) were also performed to obtain more accurate energies. The HF method at the same level computation was performed for comparing with DFT at some cases. All of the HF, DFT and NBO calculations were performed using the Gaussian 03 program package [22].

3. Results and discussion

3.1. Thermal stability

Fig. 3 shows the TG curves of the lithium organoborates in air. It can be seen that the salt decomposition starts to occur at 302 °C, 272 °C, 262 °C, and 256 °C for LBOB, 4FLBDOB, FLBDOB and LBDOB, respectively. Therefore, among the four salts LBOB exhibits the highest thermal stability while LBDOB shows the lowest. This means that the 1,2-benzenediolato-containing compound such as LBDOB decomposes easily on heating at comparatively lower temperature. Furthermore, it seems that the thermal stability depends on the higher conjugate energies of the chelate-type anion with boron [23]. The energy difference between HOMO and LUMO allow one to calculate a chemical reactivity index, the hardness (η) of these anions. Indeed, by applying Koopmans' theorem, Pearson showed that for closed-shell molecules 2η is equal to the gap between the HOMO and LUMO, i.e., $\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$. The results are listed in Table 1 and shown in Fig. 3. The LBOB holds the biggest η . According to the HSAB (Hard and Soft Acids and Bases) principle, the hard acid Li^+ prefers to coordinate with hardest base BOB^- , meaning that the most thermo stable lithium salt in the four salts is LBOB.

Compared with the previous series studies of LDFBDB, FLDFBDB and PFLDFBDB [24], the series of LBDOB, FLBDOB and 4FLBDOB have bigger η and higher thermo stabilities (Fig. 4). This means that the $\text{C}_2\text{O}_4^{2-}$ holds the higher conjugate energies of the chelate-type anion with boron than 2F^- . But the two lines are not parallel.

3.2. Solubility

Similar to LBOB, LBDOB and FLBDOB, 4FLBDOB is stable in organic electrolyte solutions but it may be decomposed by hydrolysis in aqueous solutions and converted back to their beginning reactants as shown in reaction (1). They are moderately soluble in EC + THF (1:1) with a solubility of $0.512 \text{ mol dm}^{-3}$ at 25 °C for 4FLBDOB (Table 2).

As can be seen in Table 2, the solubilities of the lithium salts in EC-based are greater than those in PC-based equimolar binary solutions. The results could be explained by the “like dissolves like” principle. All the four anions of lithium salts, BDOB^- , FBDOB^- , 4FBDOB^- , and BOB^- , have small total dipole movement. Compared

Table 1

Decomposing temperatures, energetics of anions by HF at 6-311 + + G(3df,3pd) level.

	BDOB [−]	FBDOB [−]	4FBDOB [−]	BOB [−]
$T_{\text{dec}}^{\circ}\text{C}$ (in air) [8,18,19]	256	262	272	302
HF E_{HOMO} (eV)	−4.86	−5.18	−5.86	−8.75
HF E_{LUMO} (eV)	3.04	2.99	3.83	4.32
HF η (eV)	3.95	4.08	4.84	6.54
	DFBDB [−]	FDfBDB [−]	PFDfBDB [−]	
$T_{\text{dec}}^{\circ}\text{C}$ (in air) [22]	170	185	230	
HF E_{HOMO} (eV)	−3.98	−4.32	−5.05	
HF E_{LUMO} (eV)	3.33	3.27	4.26	
HF η (eV)	3.66	3.80	4.66	

with PC, the EC hold the smaller total dipole movement. So the four lithium salts show the higher solubilities in EC than those in PC.

Compared with the previous series studies of LDFBDB, FLDFBDB and PFLDFBDB [22], the series of LBDOB, FLBDOB and 4FLBDOB have bigger total dipole movement μ and smaller solubilities in PC (Table 3).

3.3. Conductivity

Fig. 5 shows the temperature dependence of ionic conductivity of 4FLBDOB in PC solvent. We also include data for solutions in the mixed solvents of PC + THF, PC + DME, EC + THF, and EC + DME (molar ratio 1:1). A 0.10 mol dm^{-3} solution of 4FLBDOB in PC shows a conductivity of $5.02 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C. The solutions of 0.10 mol dm^{-3} 4FLBDOB in PC–DME and in EC–THF have room temperature conductivity of as high as 6.16 and $6.73 \times 10^{-3} \text{ S cm}^{-1}$, respectively, indicating that the ions in 4FLBDOB solutions are highly dissociating. On the other hand, for the saturated solutions of each lithium salt in the solvents of PC, PC + THF, PC + DME, EC + THF, and EC + DME (molar ratio 1:1), they all have a quite high conductivity of more than 5.8 mS cm^{-1} (Table 1). As can be seen in Fig. 5, the conductivity of the 0.10 mol dm^{-3} 4FLBDOB electrolyte solution in EC–THF is greater than those in the other solvents. Apparently, 4FLBDOB is highly dissociating in EC–THF mixture.

Table 4 compares the conductivities of 0.10 mol dm^{-3} 4FLBDOB solutions in PC with those of LBDOB, FLBDOB and LBDOB. It is clear that 4FLBDOB solution with the same concentration shows conductivity higher than those of FLBDOB and LBDOB solutions but lower than that of LBOB.

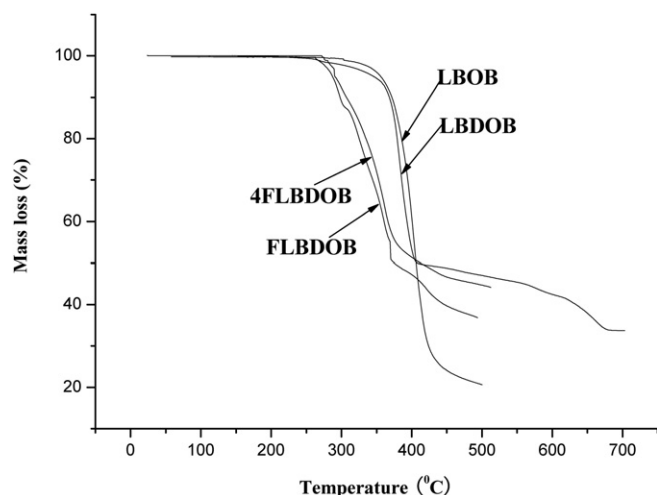


Fig. 3. TG curves of lithium organoborates at a heating rate of $5^{\circ}\text{C min}^{-1}$ in air, α -Alumina was used as a reference.

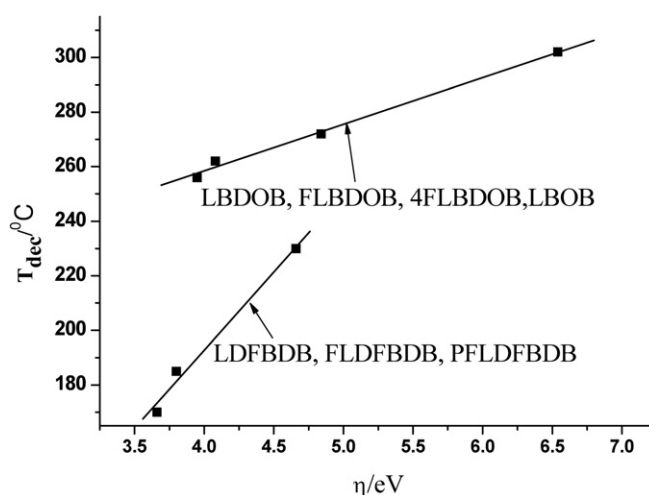


Fig. 4. Relations between the decomposition temperature (T_{dec}) of lithium salts and η of anions.

Table 2Solubility (S , mol dm⁻³) and corresponding conductivity (σ , mS cm⁻¹) of lithium salts in PC, PC- and EC-based equimolar binary solutions at 25 °C.

	PC		PC + DME		EC + DME		PC + THF		EC + THF	
	S	σ	S	σ	S	σ	S	σ	S	σ
LBDDB	0.274	5.36	0.302	6.21	0.201	4.96	0.318	5.98	0.360	6.53
FLBDDB	0.275	5.60	0.284	6.55	0.388	6.00	0.248	6.34	0.506	7.68
4FLBDDB	0.270	5.85	0.342	6.70	0.415	6.20	0.345	6.56	0.512	7.89
LBOB	0.362	6.76	0.349	7.79	0.352	6.37	0.358	7.30	0.362	8.05

Ue and Mori analyzed the contribution of the number of ions and the ion mobility to the electric conductivity for a variety of Li-ion nonaqueous electrolytes [25]. They found that the contribution from the number of free ions is generally larger than that from the ion mobility. Thus, the number of ions available plays a major role in determining the electric conductivity of a cell, and hence in the overall battery performance.

As generally recognized, the weaker the coordinating, the easier the separating of an ion pair is. With the increase of the number of F , the calculated order of binding energies is $E_{\text{bind}}(\text{LBDDB}) > E_{\text{bind}}(\text{FLBDDB}) > E_{\text{bind}}(4\text{FLBDDB}) > E_{\text{bind}}(\text{LBOB})$ (Table 4). Meanwhile, the Li–O bond length gradually becomes longer with this sequence (Table 4). Natural bond orbital (NBO) analysis is carried out to further our understanding of orbital interactions and charge delocalization. Of particular interests are the interactions between O (bounded with lithium cation) lone pairs and antibonding orbitals of lithium cation lone pair. The magnitudes of the interactions are shown in Table 4. With the increase of the number of F , it is interesting to notice that the calculated order of main orbital interaction energies (E_{int}) is $E_{\text{int}}(\text{LBDDB}) > E_{\text{int}}(\text{FLBDDB}) > E_{\text{int}}(4\text{FLBDDB}) > E_{\text{int}}(\text{LBOB})$, although E_{int} only accounts for part of E_{bind} . In fact, E_{int} may be roughly attributed to the covalency contributions to binding. Thus, the electron transfer from anion (BDOB⁻, FBDOB⁻, 4FBDOB⁻) to Li⁺ becomes lesser according to NPA and the effective cation charge becomes larger (+0.9625, +0.9628 and +0.9635 e for LBDDB, FLBDDB and 4FLBDDB, respectively). Therefore, 4FBDOB⁻ is the weakest anion of the three salts and Li⁺4FBDOB⁻ would be disassociated more than the other two salts at the same concentration of electrolyte solutions. LBOB, among the four salts, has the biggest effective cation charge (+0.9640), smallest main orbital interaction energies. Compared with the calculated data, the experimental conductivity (Table 4) increases with the effective cation charge, and decreases with E_{int} and the extent of electron transfer from anion to cation. In the series lithium salts of LDFBDB, FLDFBDB and PFLDFBDB [24], the same results has also been got as those in the series lithium salts of LBDDB, FLBDDB and 4FLBDDB.

3.4. Electrochemical stability

The electrochemical stabilities of LBOB, 4FLBDDB, FLBDDB and LBDDB solutions in PC on platinum wire electrode are shown in

Table 3

Solubility, descriptors of anions at B3LYP/6-311++G(3df,3pd) level.

	DFBDB ⁻	FDFBDB ⁻	PDFBDB ⁻
S (m, PC, 298.2k) [22]	0.518	0.443	0.306
μ /Debye	4.644	5.217	5.357
	BDOB ⁻¹	FBDOB ⁻¹	4FBDOB ⁻¹
S (m, PC, 298.2k) [18,19]	0.274	0.273 ^a	0.270
μ /Debye	6.602	7.269	7.426

^a S (m, PC, 298.2k) of FBDOB is measured again.

Fig. 6. The electrochemical oxidation potential can be obtained as ca. 4.0 V vs. Li⁺/Li for the 0.1 mol dm⁻³ solution of 4FLBDDB in PC. This is higher than the oxidation potential for LBDDB–PC solution (3.7 V) [21]. The order of the oxidation stability in these organoborates is LBOB > 4FLBDDB > FLBDDB > LBDDB, which is in the same order of the thermal stability in Fig. 3.

Electrochemical reactions can be achieved by a direct electron transfer at a certain potential. If electrons are transferred from the HOMO of a compound, a correlation is expected between the E_{HOMO} and the oxidation potential E_{ox} , because the negatives of the orbital energies in the ground state are equal to the ionization potentials according to Koopman's theorem. Several studies of anion oxidation potentials were recently updated and extended by Xue et al. [24,26]. They performed two types of calculations on the anions, obtaining HOMO energies from ab initio Hartree–Fock calculations from hybrid density functional B3LYP calculations. They have found that E_{ox} can be correlated with HOMO energies and with I_p . Similarly, in this study, the HOMO energies of different organoborate anions can be calculated using Hartree–Fock/6-311++G(3df,3pd) methods. The HOMO energies (E_{HOMO}) are found to be –8.75, –5.86, –5.18, and –4.86 eV mol⁻¹ for LBOB, 4FLBDDB, FLBDDB, and LBDDB, respectively. The electrochemical oxidation potential (E_{ox}) are found to be 4.5, 4.0, 3.9 and 3.7 V vs. Li⁺/Li for LBOB, 4FLBDDB, FLBDDB, and LBDDB, respectively. The results are given in Fig. 7, which shows a relatively good linear relationship between the HOMO energies and the limiting oxidation potentials, completely confirming the experimental result: $E_{\text{ox}}(\text{LBDDB}) < E_{\text{ox}}(\text{FLBDDB}) < E_{\text{ox}}(4\text{FLBDDB}) < E_{\text{ox}}(\text{LBOB})$. The regression result is

$$E_{\text{ox}} = 2.8622 - 0.1887 * E_{\text{HOMO}} (R = 0.984, \text{SD} = 0.074)$$

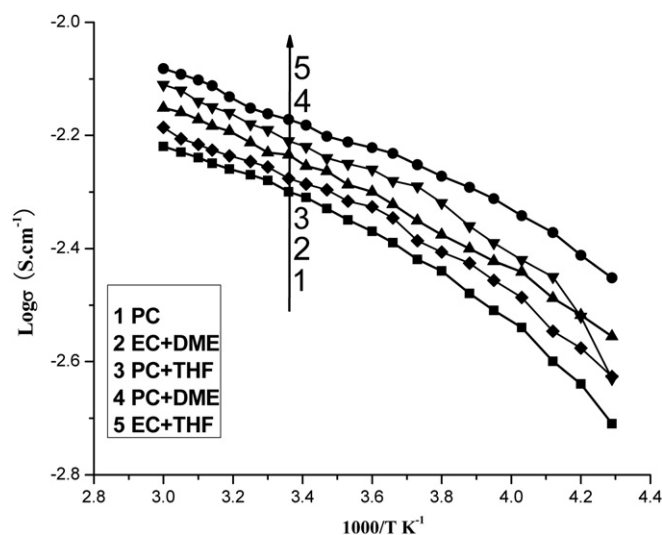


Fig. 5. Temperature dependence of ionic conductivities of 4FLBDDB solutions (0.10 mol dm⁻³) in different solvents.

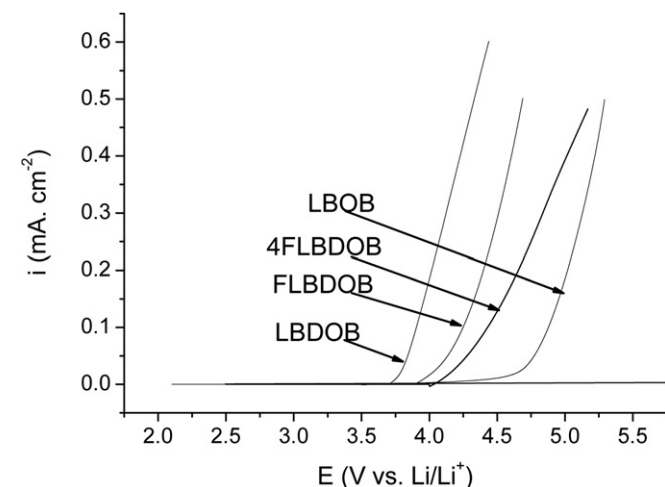
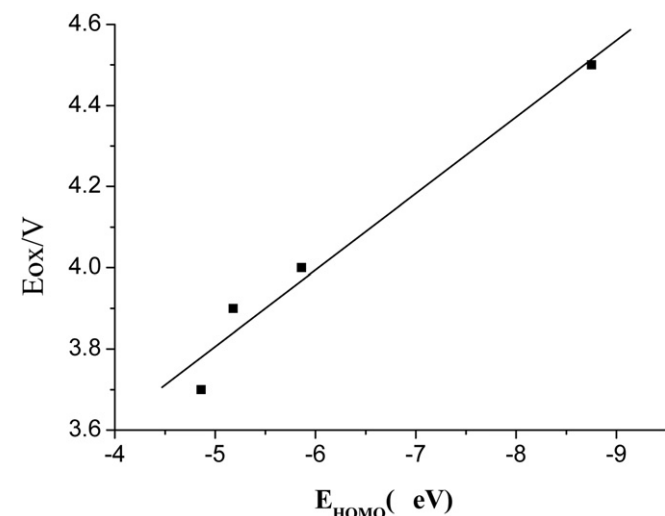
Table 4Binding energies, conductivity, NBO Energetic analysis, and Li–O bond length of the lithium ion pairs at B3LYP/6-311 ++ G(3df,3pd)//B3LYP/6-31 ++ G(2df,2p) level^a.

	Total energy (au)	Binding energy (kJ mol ⁻¹)	Conductivity (PC, 298.2k, mS cm ⁻¹)	NBO energetic analysis, E_{int} (kJ mol ⁻¹)	Li–O bond length (Å)	E_{LUMO} (eV)
LBOB	–787.167699	528	5.56	60.78	1.895	–3.32
BOB ⁻¹	–779.681725					
4FLBDOB	–1188.586134	541	5.02	61.95	1.889	–3.09
4FBDOB ⁻	–1181.095091					
FLBDOB	–890.791464	552	4.58	63.20	1.882	–2.80
FBDOB ⁻¹	–883.296146					
LBOB	–791.523613	571	4.35	63.70	1.879	–2.69
BDOB ⁻	–784.021393					

^a $E_{\text{Li}^+} = -7.284809$ (au), total energy of lithium cation is calculated at the same level.

3.5. Reduction reactivity

According to the molecular orbital theory, energy of LUMO orbital decreases and electron affinity of complexes increases [27]. The order of the ELUMO in these organoborates is LBOB > 4FLBDOB > FLBDOB > LBDOB (Table 4). With such a lower LUMO energy level, 4FLBDOB easily gets the electron for electrophilic reaction. It follows that the reduction reactivity order of central lithium-ions is LBOB > 4FLBDOB > FLBDOB > LBDOB.

**Fig. 6.** i – E curves in PC saturated solutions using a platinum wire working electrode at a scan rate of 9 mV s⁻¹ at 25 °C.**Fig. 7.** Relation between E_{ox} and E_{HOMO} of anions at DFT B3LYP/6-311 ++ G(3df,3pd) level.

4. Conclusions

A new lithium salt, lithium [tetrafluoro-1,2-benzenediolato(2-)-*o,o'* oxalato]borate (4FLBDOB), with asymmetric chelatoborate anion based on two different chelators has been synthesized. The salt, 4FLBDOB, is thermally stable and soluble in many of the common organic solvents used in batteries. The solutions are highly conductive stable. Its electrochemical oxidation potential is higher than that of FLBDOB in the common organic solvents used in batteries. A strong correlation between the HOMO energy and the electrochemical stability is established. This proves that an extensive charge delocalization, in their anions, caused by strongly electron-withdrawing anion (e.g., oxalato-, and tetrafluoro-1,2-benzenediolato-) would lower the HOMO energy, and improve the electrochemical stability of the electrolyte. Among the series of LBDOB, FLBDOB and 4FLBDOB, the new lithium salt (4FLBDOB) has the best battery performances.

Acknowledgments

This work was supported by the Chinese Academy of Sciences, Hundred Talents program and the National Science Foundation of China (grant no. 20971117 and 10979049), and 211 project of Anhui University. We are also grateful to the Solar Energy Operation Plan of Academia Sinica.

References

- [1] N. Nanbu, K. Tsuchiya, T. Shibasaki, Y. Sasaki, *Electrochem. Solid-state Lett.* 5 (9) (2002) A202.
- [2] M. Handa, M. Suzuki, J. Suzuki, H. Kanematsu, Y. Sasaki, *Electrochem. Solid-state Lett.* 2 (2) (1999) 60.
- [3] X.M. Wang, E. Yasukawa, S. Kasuya, *J. Electrochem. Soc.* 147 (7) (2000) 2421.
- [4] M.Q. Xu, A. Xiao, W.S. Li, B.L. Lucht, *Electrochem. Solid-state Lett.* 12 (2009) A155.
- [5] M.Q. Xu, A. Xiao, W.S. Li, B.L. Lucht, *J. Electrochem. Soc.* 157 (2010) A115.
- [6] J. Barthel, A. Schmid, H.J. Gores, *J. Electrochem. Soc.* 147 (1) (2000) 21.
- [7] J. Barthel, R. Buestrich, H.J. Gores, M. Schmidt, M. Wühr, *J. Electrochem. Soc.* 144 (1997) 3866.
- [8] J. Barthel, R. Buestrich, E. Carl, H.J. Gores, *J. Electrochem. Soc.* 143 (11) (1996) 3565.
- [9] J. Barthel, R. Buestrich, E. Carl, H.J. Gores, *J. Electrochem. Soc.* 143 (11) (1996) 3572.
- [10] W. Xu, C.A. Angell, *Electrochem. Solid-state Lett.* 4 (1) (2001) E1.
- [11] W. Xu, A.J. Shusterman, R. Marzke, C.A. Angell, *J. Electrochem. Soc.* 151 (4) (2004) A632.
- [12] Z.M. Xue, C.H. Chen, *Electrochim. Acta* 49 (2004) 5167.
- [13] Z.M. Xue, C.H. Chen, *Prog. Chem.* 17 (3) (2005) 399 (Chinese).
- [14] Z.M. Xue, B. Liu, C.H. Chen, *Electrochim. Acta* 51 (2006) 4554.
- [15] Z.M. Xue, J.J. Cheng, C.H. Chen, *J. Mol. Struct. Theochem.* 763 (2006) 181.
- [16] Z.M. Xue, C.H. Chen, *Mol. Simul.* 32 (2006) 401.
- [17] Z.M. Xue, C.N. Wu, B. Liu, C.H. Chen, *J. Power Sources* 171 (2007) 944.
- [18] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [19] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 270.
- [20] Z.M. Xue, C.Q. Ji, W. Zhou, C.H. Chen, *J. Power Sources* 195 (2010) 3689.
- [21] Z.M. Xue, J.F. Zhao, J. Ding, C.H. Chen, *J. Power Sources* 195 (2010) 853.
- [22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi,

- G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- [23] R.G. Pearson, Proc. Natl. Acad. Sci. U.S.A. 89 (1996) 1827.
- [24] Z.M. Xue, W. Zhou, J. Ding, C.H. Chen, Electrochim. Acta 55 (2010) 5342.
- [25] M. Ue, J. Electrochem. Soc. 141 (1994) 3336.
- [26] Z.M. Xue, X.F. Zhang, W. Zhou, C.H. Chen, J. Power Sources 202 (2012) 336.
- [27] K. Tasaki, K. Kanda, S. Nakamura, Ue. Makoto, J. Electrochem. Soc. 150 (2003) A1628.